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Ni Impurity Effects on Hydrogen Surface Chemistry and Etching of Si(111)

by

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Silane Hydrogen

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Abstract

The effect of impurity Ni on the etching of Si by hydrogen chemisorption is examined in ultrahigh vacuum with Auger electron spectroscopy and temperature programmed desorption methods. It is found that a small surface concentration of Ni ($\leq$ 5%) inhibits the production of SiH_4 from atomic H adsorption on the Si(111)-Ni surface.

I. Introduction

The interaction of chemisorbed hydrogen with Si single crystal surfaces has been studied intensely in recent years. The research has underscored the importance of Si-Si bond breaking processes (etching), resulting from the chemisorption of atomic hydrogen at low temperatures, as a means to relieve highly strained Si-Si bonds that form from surface reconstruction [1].

The interaction of chemisorbed hydrogen on heteroepitaxial metal films on silicon is also of interest for synthetically grown multilayer device structures. $NiSi_2$ films have received considerable attention because of the small lattice mismatch of $NiSi_2$ to crystalline Si; these films have been investigated using carefully controlled MBE methods [2-6]. Indeed, surface science studies have shown that small surface concentrations of Ni (~1%) are known to induce complete surface restructuring of the Si(100) [7,8] and the Si(110) surfaces [7,9]. Interestingly, other studies have shown that higher surface concentrations (~2-3%) are required for the restructuring of the Si(111) surface [7,9-11].

In this paper, we report on the interaction of chemisorbed hydrogen with Si(111)-Ni using Auger electron spectroscopy (AES) and temperature programmed desorption (TPD) methods. We find that the production of silane during a TPD experiment, normally observed from hydrogen chemisorption on Si(111)-(7x7), is precluded in the presence of very small concentrations of Ni on the Si(111) surface.

II. Experimental

A. Apparatus

The ultrahigh vacuum (UHV) system employed for this study has been

described in detail elsewhere [13]. The system is pumped with a 200 l/s ion pump, a 150 l/s turbomolecular pump, and a titanium sublimation pump. The base pressure of the system is $3x10^{-11}$ Torr and the pumping time constant is estimated to be ~0.5 s.

The apparatus is equipped with: a scanning Auger spectrometer (AES) used to establish surface cleanliness; a shielded quadrupole mass spectrometer (QMS) for line-of-sight temperature programmed desorption (TPD) studies using a small acceptance aperture; a second QMS used in some cases as an unshielded analyzer in TPD; a W-spiral filament used to dissociate H_2 gas for atomic H adsorption studies; and a digital low energy electron diffraction (LEED)/ electron stimulated desorption ion angular distribution (ESDIAD) apparatus for structural studies. Details of this apparatus have been provided elsewhere [13].

The TPD measurements on the Si(111)-Ni surface reported here were performed with the shielded QMS that was differentially pumped and fitted with an acceptance aperture (5.0 mm diameter) so that only desorbing species originating from the center of the crystal were observed [13].

The crystals used in this study were cut from a p-type, B doped, 10 Ω cm Czochralski grown Si(111) boule. The 150 mm diameter wafers were sliced (0.15 cm thick) from the boule, oriented to within ~1°, and commercially polished. The wafers were then diced into approximate square geometry (1.30 cm x 1.31 cm). For mounting in UHV, the crystal edges were slotted on all four edges with a diamond string saw to produce 0.4 mm slots that were 1.5 mm deep. Tantalum tabs, which are attached to two tungsten support leads, are then spring loaded into the slots [13,14]. Programmed heating was accomplished by resistively heating the crystal with a temperature controller equipped with a power feedback loop [15]. The crystal support was cooled with N_2 gas that first passes through a liquid nitrogen reservoir before reaching the crystal support assembly. This

mounting procedure permitted exceptionally uniform heating and cooling and resulted in a controlled crystal temperature range from 120 K to 1200 K.

The measurement of the crystal temperature was accomplished with a thermocouple (chromel-constantan, type-E) that was encased in a Ta foil envelope and inserted into the slot on the top edge of the crystal. This is shown in Fig. 1. Because of the possibility of Ni contamination from the thermocouple, care is taken to ensure that the thermocouple wires do not come in contact directly with the Si crystal. The intimate contact of the thermocouple with the Si crystal was established with a W wire spring clip that spanned the rear surface of the Si(111) crystal and was inserted into the top and bottom slots.

B. Crystal Preparation Methods Leading to Ni Incorporation

Crystal preparation was achieved by Ar^+ ion bombardment (2 keV, 2 $\mu A/cm^2$, 15 min.) at glancing incidence (70° from normal). The purity of the Si(111) surface was measured using Auger spectroscopy. The Ni is present as an impurity in our crystal, and considerable effort was made in establishing the source of the impurity. It is well known that contact with stainless steels can induce transition metal impurities during the handling of Si [16,17]. Extreme care was taken in the handling of the crystals to avoid such contamination. For example, teflon forceps and containers were used during transport and mounting of the crystals. High purity Ta sheet was also used for the mounting material and AES investigations of the Ta revealed no Ni impurity within the depth of analysis.

We found that there were two sources of Ni. Perhaps the most obvious source is the thermocouple wire assembly, shown in Fig. 1. By careful inspection of the spot weld used to attach the thermocouple to the Ta envelope, we found that small perforations through the Ta may occur on occasion, thus

providing an intermittent source of Ni after mounting a fresh crystal. Ni is known to react with Si at room temperature [2,3,6], and Ni diffusion has been readily observed by others [7,9,18,19] in the temperature regime used in these studies. The second source of Ni was determined to be the residual Ni left over from the cutting of the polished wafer material- either in the dicing or the slotting procedures in which diamond-impregnated stainless steel cutting tools are used. Other possible sources such as ion bombardment/sputtering of nearby surfaces or impurities in the Ta clip material were considered and were shown in careful control experiments not to be sources of impurity Ni.

The typical derivative Auger spectrum of a crystal, after insertion into the UHV chamber and a 200°C bakeout (12 hours), is shown in Fig. 2(a). A large O (KLL) feature at 508 eV and a large C (KLL) feature at 270 eV is clearly observed, in addition to the attenuated 91 eV Si(LVV) peak. Such a spectrum is typical of an unprepared Si crystal with a nascent oxide layer. In particular no Ni (LMM) 848 eV AES feature is observed within the noise limit.

Heating the crystal to 1173 K for ~5 min results in the removal of the surface oxide layer, as shown in Fig. 2(b). A residual C feature is detected. In addition, a Ni (MNN) feature at 60 eV and the 848 eV (LMM) feature are clearly observed. (The 716 eV and the 783 eV features are also due to Ni (LMM) transition [20]). The C impurity can be completely removed by Ar^+ ion bombardment as determined by AES. The Ni impurity, however, could only be temporarily removed by Ar^+ ion bombardment; subsequent annealing restored the Ni features in the AES spectrum suggesting that the source of surface Ni was from the bulk Si. Attempts to remove the Ni contamination by thermal annealing and ion bombardment at various crystal temperatures were unsuccessful. Auger studies of the crystal surface after ion bombardment and prior to annealing showed no evidence of Ni contamination from the bombardment procedure.

The atomic fraction of impurity Ni typically present (within the depth of Auger sampling) was ~5%, as determined from the AES peak-to-peak heights of the Si(LVV, 92 eV) and the Ni(LMM, 848 eV) Auger features, throughout the work reported here. Suitable sensitivity factors were used to determine the atomic fraction of the surface Ni [20,21]. The well known ($\sqrt{19}$x$\sqrt{19}$)R23.5° structure [22,23], which is characteristic of Ni-contaminated Si(111), was easily observed with our digital LEED apparatus at these concentrations.

C. Removal of the Surface Ni Impurity

We found that the removal of the tenacious Ni impurity could be accomplished by treating the crystal prior to insertion into UHV with the well-known peroxide/HF stripping procedure [15] after all of the cutting and slotting has been done. Careful spot welding of the Ta foil envelope used to encase the thermocouple is also important: no perforations in the Ta can be made. A second layer of Ta applied as a barrier between the welded envelope and the Si crystal easily avoids this problem.

D. Adsorption of Atomic H

The adsorption of atomic hydrogen was accomplished by introducing H_2 gas into the chamber ($P(H_2)$~10^{-8} Torr), and placing the prepared crystal surface ~4 cm from a hot (T=1800 K) W spiral filament. Crystal temperatures during atomic hydrogen exposures were kept to ~340 K by cooling the support structure as described above. The crystal was biased at -100V during the atomic hydrogen exposures to avoid possible ESD effects from stray electrons. Atomic H exposures are reported in Langmuirs ($1L=10^{-6}$ Torr sec) of H_2 (uncorrected for ionization gauge sensitivity) and atomic H exposures were found to be proportional to H_2 exposures.

III. Results and Discussion

A. Hydrogen Desorption from Si(111) and Si(111)-Ni

The TPD measurements of hydrogen from H+Si(111)-(7x7) and H+Si(111)-Ni are shown in Fig. 3 for comparison. The β_3- (T_{max}~400 K), β_2- (T_{max}~650 K), and β_1-H_2 (T_{max}~775 K) desorption features from H+Si(111)-(7x7) are observed in the upper panel of Fig. 3, and indicate the formation of tri-, di- and monhydride surface species respectively [1]. These TPD measurements were made using the unshielded QMS. An exposure of 21 L H_2 was observed to saturate the growth of the β_2- and β_1-H_2 desorption features under the experimental conditions described above. The formation of the polyhydride β_3- and β_2-H_2 phases on the Si surface necessarily involves the scission of Si-Si bonds. This bond breaking is known to induce surface disorder and to be accompanied by the desorption of silane causing removal of Si atoms from the surface [1].

The lower panel of Fig. 3 shows the hydrogen thermal desorption from H+Si(111)-Ni and were obtained with the shielded QMS. Again three features are seen at (β_3') T_{max}~400 K, (β_2') T_{max}~600 K, and (β_1') T_{max}~725 K. It is noted that the β_1' and β_2' desorption features are shifted downward by ~50 K relative to the H_2 desorption observed from H + Si(111)-(7x7).

B. SiH_4 Desorption from Si(111) and Si(111)-Ni

The thermal desorption of SiH_4 is observed (by the fragmentation product SiH_3^+ TPD signal, Fig. 4, upper panel) from the chemisorption of atomic H on Si(111)-(7x7) in agreement with other work [24]. The other TPD fragmentation products of silane observed are SiH^+ and SiH_2^+ and these are not shown here. It is seen that the desorption of silane is initially observed at atomic H coverages where the β_3- and β_2-H_2 desorption states are initially populated

(at ~5 ' H_2 exposure under these conditions in our apparatus).

The presence of a small concentration (~5%) of Ni on the Si(111) surface clearly affects the production of silane and this is shown in Fig. 4 (lower panel). For all atomic H exposures reported here, the silane desorption channel is effectively closed and this indicates that the production of silane is not favored on such a surface. It is remarkable that the small 5% surface concentration of Ni present on the Si(111) surface strongly decreases the ability of adsorbed H to produce SiH_4. Others have shown that the catalytic properties of metal surfaces are an important consideration in silane surface chemistry [25,26].

The results of Fig. 4 suggest that the presence of Ni may induce a stability to the reconstructed surface that precludes the usual Si-Si bond scission observed from the chemisorption of H on clean Si(111)-(7x7). Such Si-Si bond breaking, resulting from the chemisorption of atomic H and leading ultimately to SiH_4(g) production, has been suggested as a means for the surface to relieve the highly-strained backbonds in the adatoms [27]. The Ni impurity-stabilized Si(111) surface reconstruction has been investigated by others [6,11].

The SiH_3(a) species has been observed by Jansson and Uram using infrared spectroscopy from the adsorption of atomic hydrogen on Si(111) in the 100 to 400 K temperature regime [28]. The work of Greenlief, et al. has also suggested that the SiH_3(a) species is a precursor species to SiH_4(g) [29]. Therefore, a study of Fig. 3 where an increase in the β_3'-H_2 desorption yield is observed indicates that in the case of H + Si(111)-Ni one would expect enhanced SiH_4(g) production. However, inspection of Fig. 4(b) reveals that this is clearly not the case. Assuming that β_3'-H_2 from Si(111)-Ni is also related to SiH_3(a) species, we conclude that Ni prevents the conversion of SiH_3(a) to SiH_4(g). It

.s interesting to note in connection to our observations that the decomposition of silane on Ni(100) occurs readily at ~250K, leaving Si on the Ni(100) surface and producing gas phase hydrogen [25].

IV. Summary

We have found that small concentrations of impurity Ni on the Si(111) surface inhibit the production of silane and therefore the subsequent removal of Si atoms (etching) from the surface. This is accompanied by changes in the thermal desorption behavior of hydrogen.

V. Acknowledgements

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Figure Captions

Figure 1. Cross section of the slotted Si(111) crystal showing the thermocouple mounting technique.

Figure 2. Typical Auger spectra of the Si(111) crystal (a) after installation and baking in UHV; and (b) after annealing the crystal to 1173 K followed by cooling to 120 K. The electron beam energy used in AES studies is 3 keV, with a 2μA beam current in a 0.5mm diameter spot. Modulation voltage is V_{mod}=5 V p-p.

Figure 3. H_2 desorption from atomic H chemisorption on clean Si(111)-(7x7) ((a) upper panel) and Si(111)-($\sqrt{19}$x$\sqrt{19}$)-Ni ((b) lower panel). The spectra in (a) were obtained with the unshielded QMS; those in (b) with the shielded QMS.

Figure 4. SiH_4 thermal desorption from atomic H chemisorption on clean Si(111)-(7x7) ((a) upper panel) and Si(111)-($\sqrt{19}$x$\sqrt{19}$)-Ni ((b) lower panel). The presence of impurity Ni strongly inhibits the formation of SiH_4(g). The spectra in (a) were obtained with the unshielded QMS; those in (b) with the shielded QMS (see Fig. 3).

Cross Section of Slotted Si(111) Crystal-Thermocouple Mounting Technique

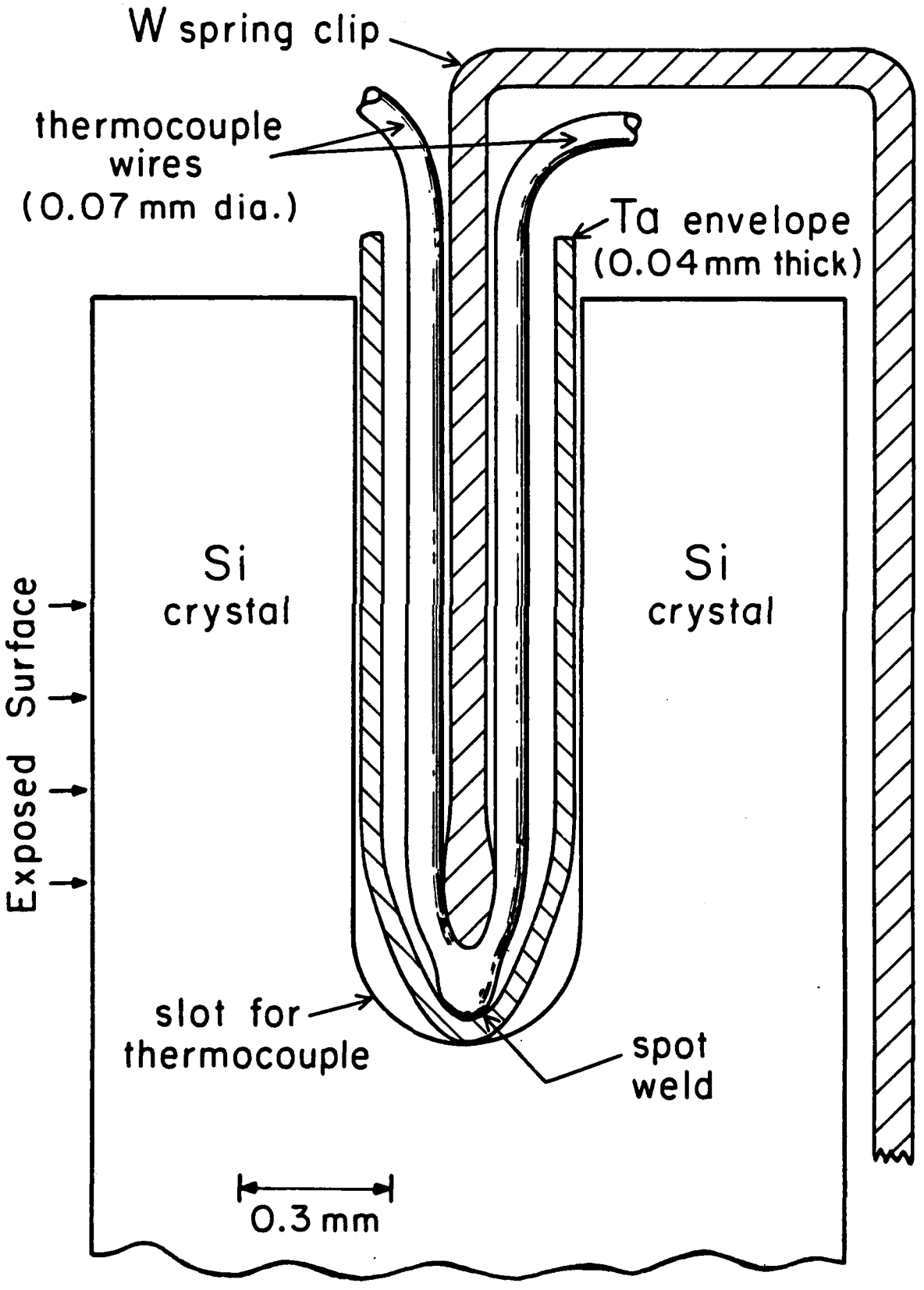

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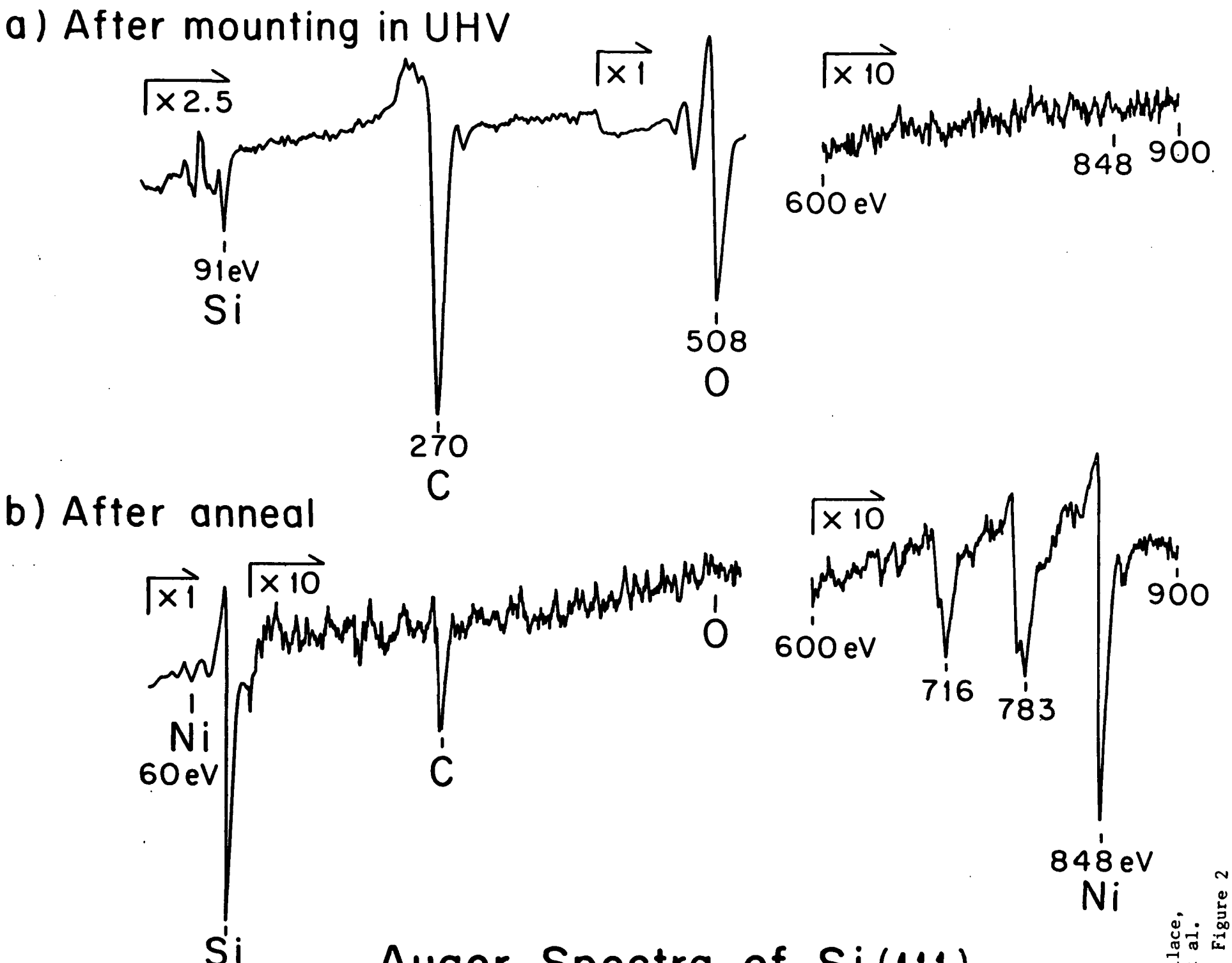
Figure 1



Auger Spectra of Si(111)

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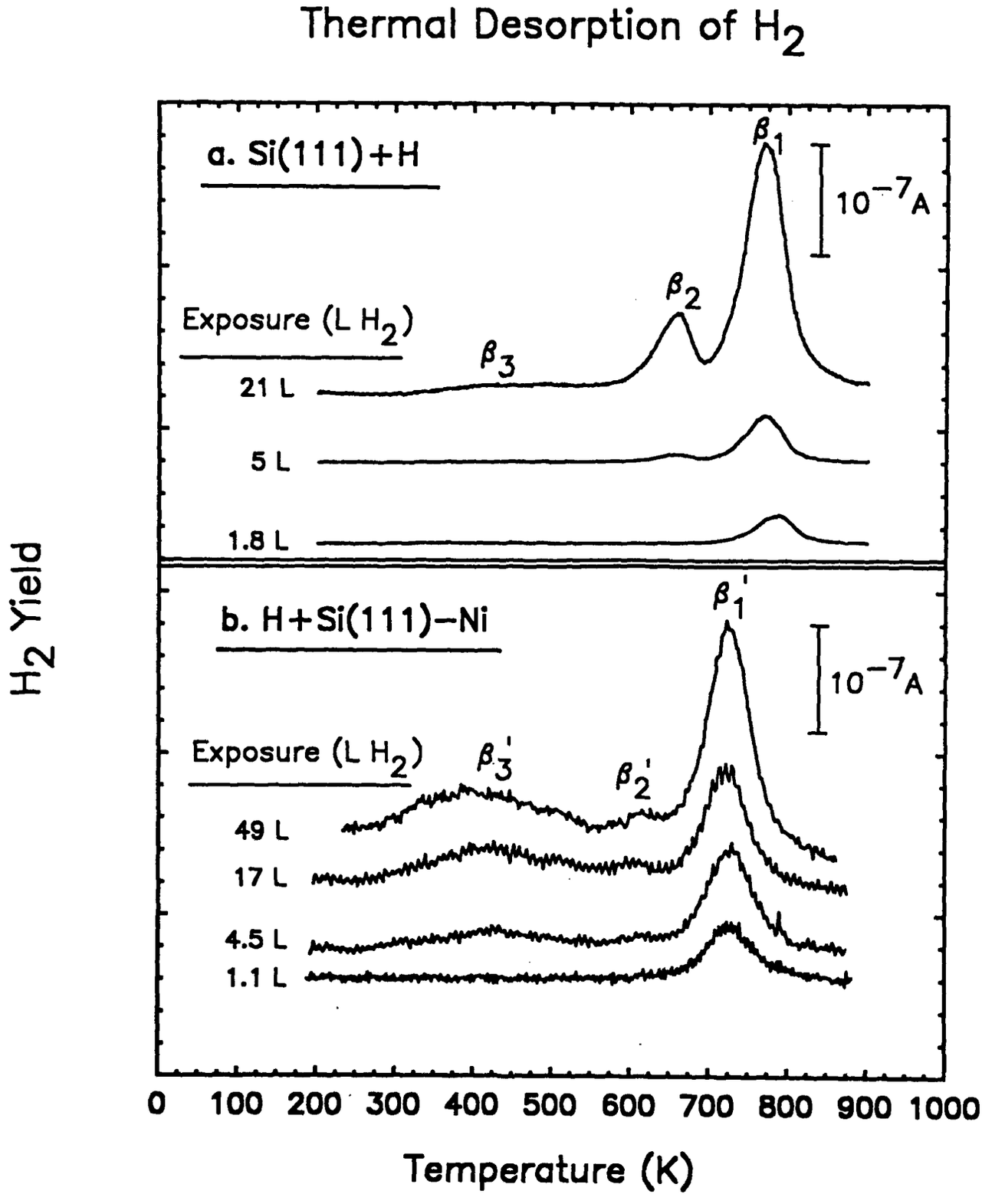

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Figure

Thermal Desorption of SiH_4

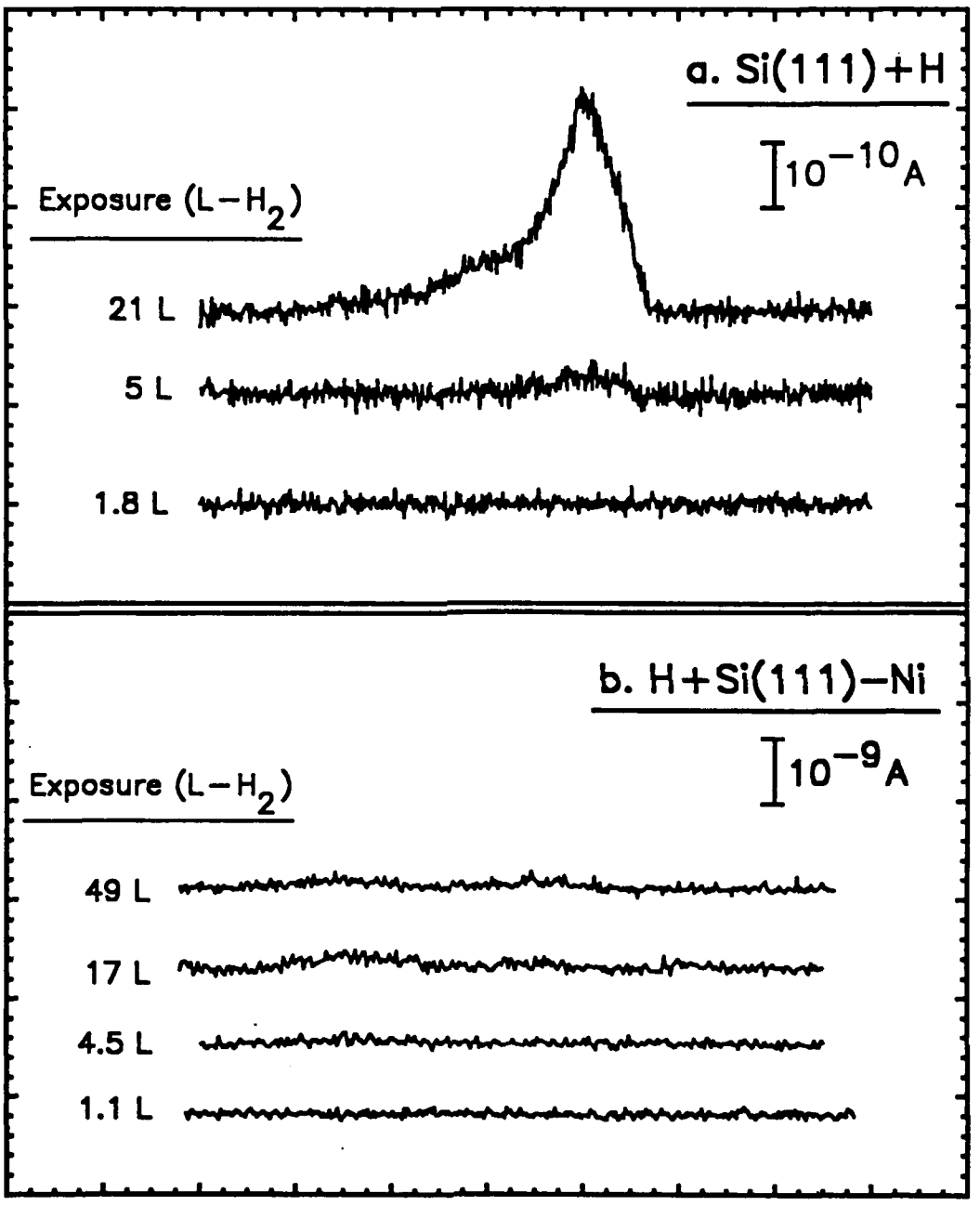

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Figure 4

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